EFFECT OF ADDITION OF SALTS ON COAL EXTRACTION IN CS_2/NMP MIXED SOLVENT

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ABSTRACT

The effect of addition of various salts on the extraction of seven different kinds of coals with carbon disulfide-*N*-methyl-2-pyrrolidinone (CS_2-NMP) mixed solvent (1:1 by volume) was investigated. Addition of some salts considerably increased the extraction yield for several coals. For Upper Freeport coal, in particular, the addition of a very small amount (0.25 mol/kg-coal) of tetrabutylammoniumfluoride increased the extraction yield from 60 to 84%. The effect of a kind of anions on the extraction yield was also examined. It was found that the charge density of anion is responsible for the increase of the extraction yields. The fractionations of the extracts using pyridine indicate that the extracts obtained with the additive contain heavier constituents than those without the additive.

INTRODUCTION

The extraction of bituminous coals with CS_2/NMP mixed solvent (1:1 by volume) was found to give very high extraction yields at room temperature. [1] It was also observed that the addition of a small amount of electron acceptors such as tetracyanoethylene (TCNE) and 7,7,8,8-Tetracyanoquinodimethane (TCNQ) to the mixed solvent increases the extraction yields significantly. [2,3] For example, the yield of the room temperature extraction of Upper Freeport coal with the 1:1 mixtures of CS_2/NMP increases from 59 to 85 wt% (dry-ash-free basis) by adding only 5 wt% (based on coal) of TCNE to the solvent. [2] The effects of addition of TCNE are reversible. [4] Hence the increase of the extraction yield was found to be not due to the breakage of covalent bonds such as ether bonds in coal but due to the suppression of the association between coal macromolecules via non-covalent bonds. Previous studies on the mechanism for enhancing coal solubility have been concentrated on the charge-transfer complex formation between additives and coal. However the correlation between the solubility of coal and the electron acceptability was rather poor. Furthermore EPR studies of Illinois No.6 coal demonstrate that the increase in the spin concentration by the addition of electron acceptors is not due to the formations of new paramagnetic centers, i.e., thermally accessible triplet state arising from charge-transfer interactions. [5] Thus the formation of the charge transfer complex between the coal and the electron acceptor does not seem to be the plausible mechanism for enhancing coal solubilities. Recently, Chen and Iino proposed another possible explanation for the effect of additives on coal extraction. [6,7] It was found that TCNE does not exist as a neutral molecule in NMP as well as in the NMP/CS_2 mixed solvent but forms TCNE anion derivative, i.e., NMP 1,1,2,,3-pentacyanopropene salt (NPCNP). It has been well known that TCNE easily generate PCNP anion by reacting with aprotic polar solvent such as pyridine [8] or pyridone [9,10] in the presence of the proton source like water. They also examined that the effect of addition of NPCNP on the extraction yields of UF coal with CS_2/NMP mixed solvent. The addition of 0.2 mol/kg-coal NPCNP increases the extraction yield from 59 to 72 wt%, which is comparable to the increment by adding the same amount of TCNE. These observations indicate that the anion plays a key role on the enhancement of the coal solubility. However there is little information available on what kinds of anion is effective for the coal extractions. Furthermore, the effect of additives on the solvent properties such as the Gutmanns donor (DN) and acceptor numbers has not been focused yet.

In the present study, the effect of anion on the coal extraction with CS_2/NMP mixed solvent is examined using tetrabutylanmonium and lithium salts of various anions systematically. The changes in the bulk property of the solvent with adding salts are also examined based on the solvatochromism of well-characterized probe dye indicators. [11,12]

EXPERIMENTAL

Solvent extraction. Seven different kinds of coals were used as coal samples. Their particle sizes were finer than 150 μm. They were dried under vacuum at 353 K for 12 h. The elemental composition of the coal samples are listed in Table 1. 1.0 g of a coal sample was extracted with 60 mL of CS_2/NMP mixed solvent (1:1 by volume) with or without the additive under ultrasonic (38 kHz) irradiation for 30 min at room temperature. The mixtures were subsequently centrifuged under 29000 g for 60 min, and the supernatant was immediately filtered thorough a membrane paper with a pore size of 0.8 μm. The residue was repeatedly extracted with the fresh mixed solvent in the same way, until the filtrate become almost colorless. This exhaustive extraction usually needs the repeating of 4-6 times. The residue was thoroughly washed with acetone to remove CS_2 and NMP retained. Extraction yields were determined on a dry ash free basis from the amount of the residue. The extract, hereafter referred to as MS was further fractionated using acetone and pyridine to yield acetone soluble (AS), pyridine soluble / acetone insoluble (PS), and pyridine insoluble (PI) fractions, respectively. Detailed extraction and fractionation procedures were described in elsewhere. [1] Several kinds of tetrabutylanmonium and lithium salts were used as additives. Typical amount of the additive was 0.25 mol/kg coal.

Solvatochromism. The effect of addition of LiCl on the DN of NMP was empirically evaluated by using copper(II)-*N,N,N',N'*-tetramethylethylendiamine-acetylacetonate $(Cu(tmen)(acac)^+)$. The probe dye indicator was dissolved in the NMP/LiCl solvent, and the mixture was subjected immediately to the UV/VIS measurements. The DN was calculated using an empirical equation based on the absorption band of the dye in the solvent. [12]

RESULTS AND DISCUSSION

Effects of addition of the salts on the extraction yields of UF coals are shown in Table 2. The extraction yields varies with the types of salts. TBAF affects the coal extraction most significantly and increased the yield up to 84%. The results for the halogenide salts indicate that a kind of halogenide anions affects the extraction yields. The yields increased in the order, $F^- > Cl^- > Br^- > I^-$. This indicates that the anions with the small ion radius or large elecronegativity are effective for the enhancement of the yield. Lewis acidity or basicity of ions can be categorized reasonably by HASB (Hard and Soft Acids and Bases) principle of Pearson. [13] He proposed a simple, useful rule, that is, hard acids bind strongly to hard bases and soft acids bind strongly to soft bases. It is convenient to divide bases into two categories, those that are polarizable (low charge density), or "soft," and those that are nonpolarizable (high charge density), or "hard." F^- and Cl^- are categorized into hard base, while Br^- and I^- are soft base. Hard base tends to attract proton strongly. If we use protic solvents, F^- and Cl^- must be strongly solvated and would show little effect on the extraction. Because the CS_2/NMP mixed solvent is dipolar, aprotic solvent, these anion would be solvated weakly and can interact with some hard acidic sites in coal. Acid - base interaction between coal and anion would be responsible for the enhancement of the extraction yields. On the other hand, soft base such as Br^- and I^- is strongly solvated since the dipolar aprotic solvent such as the mixed solvent can be categorized into soft acid solvent. Hence these soft base can not interact with the coal and have little effect. Non-halogenide anions such as CH_3COO^-, ClO_4^-, and NO_3^- were also used. CH_3COO^- is hard base and increases the extraction yield while others are soft base and the effects are less significant.

Table 3 lists the effect of TBAF addition on the extraction yields of several kinds of coals. Upper Freeport, Lower Kittanning, and Stigler coals are increased their extraction yields with the mixed solvent by the addition of TBAF, but for Pittsburgh No.8, Illinoi No.6 coals the yields did not increase. For the addition of TCNE the same tendency of the extraction yields was obtained for the above-mentioned five coals. The results of the fractionation of MS of Upper Freeport coal are shown in Table 4. The increase in the MS yields is mainly due to the increase of the heaviest extract fraction, i.e., PI, and little increase in the lighter fraction of AS and PS. Figure 1 shows the experimental procedure for examination of the reversibility of the effect of additive on the extraction yields of UF coal. The yield of MS obtained from the extraction with LiCl is 78 wt %. The MS was washed exhaustively with acetone/water mixed solvent (1:4 by volume) to remove LiCl retained, and subsequently extracted with the CS_2-NMP mixed solvent in the absence of LiCl. A portion of MS became again insoluble, i.e., 63 wt % of UF coal is extracted by the mixed solvent. The yield was almost same as the yield of MS obtained without additives. Hence the effects of addition of LiCl seem to be reversible as observed for the addition of TCNE.

Figure 2 shows the effect of LiCl concentration in NMP on the DN of NMP as well as extraction yield with NMP for UF coal. DN of NMP is rapidly increased from 27 to 54 even by the addition of very small amount of LiCl (10 mmol/L) and kept constant value above 10 mmol/L. The extraction yield is also increased by LiCl addition, it increases with increasing the concentration of LiCl up to 120 mmol/L. The increase in the extraction yield is observed even where the DN is almost constant, indicating that the effect of the salt additive on the coal extraction can not be explained only by the change in the bulk property of solvent with salt addition. It is necessary to consider the interaction between coal and anion more in detail.

CONCLUSIONS

The effect of addition of various salts on the extraction of seven different kinds of coals with carbon disulfide-*N*-methyl-2-pyrrolidinone (CS_2-NMP) mixed solvent (1:1 by volume) was investigated. Addition of some salts considerably increased the extraction yield for several coals. For Upper Freeport coal, in particular, the addition of a very small amount, 0.25 mol/kg-coal of tetrabutylammoniumfluoride increased the extraction yield from 60 to 84%. The effect of a kind of anions on the extraction yield was also examined. It was found that the charge density of anion seems to be responsible for the increase in the extraction yields. The fractionations of the extracts using pyridine indicate that the extracts obtained with the additive contain heavier constituents than those without the additive.

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REFERENCES

(1) Iino, M.; Takanohashi, T.; Osuga, H.; Toda, K. *Fuel* **1988**, *67*, 1639.
(2) Liu, H.; Ishizuka, T.; Takanohashi, T.; Iino, M. *Energy Fuels* **1993**, *7*, 1108.
(3) Ishizuka, T.; Takanohashi, T.; Ito, O.; Iino, M. *Fuel* **1993**, *72*, 579.
(4) Iino, M.; Liu, H.; Hosaka, N.; Kurose, H.; Takanohashi, T. *Prepr. Pap. Am. Chem. Soc., Div. Fuel. Chem.* **1997**, *42(1)*, 248.
(5) Thompson, R. T., Rothenberger,K.S.,Retcofsky,H.L. *Energy Fuels* **1997**, *11*, 739.
(6) Chen, C.; Kurose, H.; Iino, M. *Energy Fuels* **1999**, *13*, 1180.
(7) Chen, C.; Iino, M. *Energy Fuels* **1999**, *13*, 1105.
(8) Middleton, W. J.; Little, E. L.; Coffman, D. D.; Engelhardt, V. A. *J. Am. Chem. Soc.* **1958**, *80*, 2795.
(9) Thyagarajan, B. S.; Rajagopalan, K.; Gopalakrishnan, P. V. *Chem. Ind.* **1966**, *5*, 1887.
(10) Thyagarajan, B. S.; Rajagopalan, K.; Gopalakrishnan, P. V. *J. Chem. Soc. (B)* **1968**, 300.
(11) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.
(12) Spange, S.; Reuter, A.; Vilsmeier, E.; Heinze, T.; Keutel, D.; Linert, W. *J. Polymer Sci. Part A* **1998**, *36*, 1945.
(13) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

Table 1. Properties of Coal Samples

Coal	Symbol	Ultimate analysis(wt%,daf)				Ash(wt%,db)
		C	H	N	O+S[a]	
Sewell'B'	SW	88.4	5.3	1.4	4.9	4.6
Upper Freeport	UF	86.2	5.1	1.9	6.8	13.1
Lower Kittanning	LK	84.0	5.6	1.7	8.7	9.0
Lewiston Stockton	LS	82.9	5.4	2.0	9.7	19.6
Pittsburgh No.8	PB	82.6	5.5	2.1	9.8	8.7
Stigler	SG	77.8	4.8	1.5	15.9	11.7
Illinois No.6	IL	76.9	5.5	1.9	15.7	15.0

[a] By difference

Table 2. Effect of Salt Types on Extraction Yields [a] of UF Coal

Additive [b]	Extraction yield (wt%,daf)
LiCl	78.1
LiBr [c]	68.7
LiI [d]	60.9
$(n\text{-Bu})_4N^+F^-$	83.9
$(n\text{-Bu})_4N^+Cl^-$	78.8
$(n\text{-Bu})_4N^+Br^-$	61.8
$(n\text{-Bu})_4N^+I^-$	59.3
$(n\text{-Bu})_4N^+OCOCH_3^-$	75.6
$(n\text{-Bu})_4N^+ClO_4^-$	62.1
$(n\text{-Bu})_4N^+NO_3^-$	54.0
None	59.8

[a] CS_2-NMP mixed solvent (1:1 by volume), room temperature

[b] 0.25mol/kg-coal [c] 0.95mol/kg-coal

[d] 1.87mol/kg-coal

Table 3. Effect of TBAF [a] Addition on Extraction Yields [b] of Coals

Coal	C% (dry ash free)	Extraction yield (wt%, daf) None	Extraction yield (wt%, daf) 0.25mol/kg-coal
SW	88.4	33.9	48.0
UF	86.2	59.8	83.9
LK	84.0	38.0	61.6
LS	82.9	25.6	25.8
PB	82.6	37.8	37.4
SG	77.8	26.0	72.2
IL	76.9	24.6	25.5

[a] $(n\text{-Bu})_4N^+F^-$

[b] CS_2-NMP mixed solvent (1:1 by volume), room temperature

Table 4. Effect of TBAF [a] Addition on Extraction Yields [b] of Coals and Fraction Distributions of the Extracts

Coal	TBAF	Extraction yield (wt%,daf)	Fraction distribution(wt%,daf) AS	PS	PI
UF	None	60.1	8.2	25.0	26.9
	0.25mol/kg-coal	82.4	11.5	12.7	58.2
LK	None	38.7	6.3	27.1	5.3
	0.25mol/kg-coal	63.7	9.4	17.9	36.4
PB	None	43.5	12.3	30.0	1.2
	0.25mol/kg-coal	39.9	11.8	23.4	4.7
SG	None	21.2	6.1	14.5	0.6
	0.25mol/kg-coal	62.4	6.4	17.2	38.8
IL	None	27.9	7.8	19.1	1.0
	0.25mol/kg-coal	27.4	10.0	16.8	0.6

[a] $(n\text{-Bu})_4N^+F^-$

[b] CS_2-NMP mixed solvent(1:1 by volume), room temperature

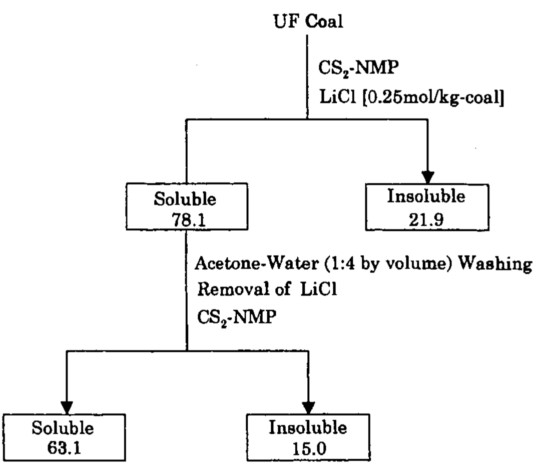

Fig. 1. Reversibility of the Effect of LiCl Addition on the Extraction,Yield

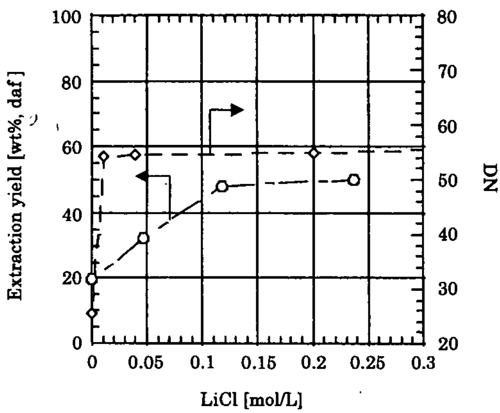

Fig. 2. Effect of LiCl concentration on DN of NMP as well as the Extraction Yield of UF Coal